

A FREE-BOUNDARY PROBLEM FOR CONCRETE CARBONATION: RIGOROUS JUSTIFICATION OF THE \sqrt{t} -LAW OF PROPAGATION

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Abstract. We study a one-dimensional free-boundary problem describing the penetration of carbonation fronts (free reaction-triggered interfaces) in concrete. A couple of decades ago, it was observed experimentally that the penetration depth versus time curve (say $s(t)$ vs. t) behaves like $s(t) = C\sqrt{t}$ for sufficiently large times $t > 0$ (with C a positive constant). Consequently, many fitting arguments solely based on this experimental law were used to predict the large-time behavior of carbonation fronts in real structures, a theoretical justification of the \sqrt{t} -law being lacking until now.

The aim of this paper is to fill this gap by justifying rigorously the experimentally guessed asymptotic behavior. We have previously proven the upper bound $s(t) \leq C'\sqrt{t}$ for some constant C' ; now we show the optimality of the rate by proving the right nontrivial lower estimate, i.e. there exists $C'' > 0$ such that $s(t) \geq C''\sqrt{t}$. Additionally, we obtain weak solutions to the free-boundary problem for the case when the measure of the initial domain vanishes. In this way, our mathematical model is now allowing for the appearance of a moving carbonation front – a scenario that until was hard to handle from the analysis point of view.

Key words. Free-boundary problem, concrete carbonation, large-time behavior, \sqrt{t} -law of propagation, appearance of a carbonation front, phase change;

AMS subject classifications. 35R35, 35B40, 80A22

1. Introduction.

1.1. Background. Environmental impact on concrete parts of buildings results in a variety of unwanted chemical and chemically-induced mechanical changes. The bulk of these changes leads to damaging and destabilization of the concrete itself or of the reinforcement embedded in the concrete. One important destabilization factor is the drop in pH near the steel bars induced by carbonation of the alkaline constituents; see for instance [12, 13, 22] and [20] for technical details and [14, 2] for an introduction to the mathematical modeling of the situation¹. The destabilization is caused by atmospheric carbon dioxide diffusing in the dry parts and reacting in the wet parts of the concrete pores. The phenomenon is considered as one of the major processes inducing corrosion in concrete. A particular feature of carbonation is the formation of macroscopic sharp reaction interfaces or thin reaction layers that progress into the unsaturated concrete-based materials. The deeper cause for the formation of these patterns is not quite clear, although the major chemical and physical reasons seem to be known.

Mathematically, the proposed model is a coupled system of semi-linear partial differential equations posed in a single 1D moving domains. The moving interface (front position in 1D) is assumed to be triggered by a fast chemical reaction – the carbonation reaction. Non-linear transmission conditions of Rankine-Hugoniot type are imposed across the inner boundary that separates the carbonated regions from

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¹Remotely related mathematical approaches of similar reaction-diffusion scenarios have been reported, for instance, in [10, 9, 6].

the uncarbonated ones. The movement of the carbonated region is determined via a non-local dynamics law.

The key objective is not only to understand the movement of a macroscopic sharp reaction front in concrete but rather to *predict the penetration depth after a sufficient large time*.

A couple of decades ago, it was observed experimentally that the penetration depth versus time curve (say $s(t)$ vs. t) behaves like $s(t) = C\sqrt{t}$ for sufficiently large times $t > 0$ (with C a positive constant). Consequently, many fitting arguments solely based on this experimental law were used to predict the large-time behavior of carbonation fronts in real structures, a theoretical justification of the \sqrt{t} -law being lacking until now.

This is the place where our paper contributes: We want to fill this gap by justifying rigorously the experimentally guessed asymptotic behavior.

1.2. Basic carbonation scenario—a moving one-phase approach. We study a one-dimensional free boundary problem system arising in the modeling of concrete carbonation problem. We consider that the concrete occupies the infinite interval $(0, \infty)$ and that there exists a sharp interface $x = s(t)$, $t > 0$ separating the carbonated from the uncarbonated zone. The whole process can be seen as a solid-solid phase change; see the two colors in Fig. 1.1 (left). One color points out to $CaCO_3$ (carbonated phase), while the other one indicates $Ca(OH)_2$ (uncarbonated phase). The zone of interest is only one of the solid phases, namely the carbonated zone. We denote it by $Q_s(T)$ and, in mathematical terms, this is defined by $Q_s(T) := \{(t, x) : 0 < t < T, 0 < x < s(t)\}$ for some $T > 0$. Throughout this paper u and v denote the mass concentrations of CO_2 in air and water, respectively. As mentioned in [2], s , u and v satisfy the following system $P = P(s_0, u_0, v_0, g, h)$ (1.1) \sim (1.7):

$$(1.1) \quad u_t - (\kappa_1 u_x)_x = f(u, v) \quad \text{in } Q_s(T),$$

$$(1.2) \quad v_t - (\kappa_2 v_x)_x = -f(u, v) \quad \text{in } Q_s(T),$$

$$(1.3) \quad u(t, 0) = g(t), v(t, 0) = h(t) \quad \text{for } 0 \leq t \leq T,$$

$$(1.4) \quad s'(t) = \psi(u(t, s(t))) \quad \text{for } 0 < t < T,$$

$$(1.5) \quad -\kappa_1 u_x(t, s(t)) = \psi(u(t, s(t))) + s'(t)u(t, s(t)) \quad \text{for } 0 < t < T,$$

$$(1.6) \quad -\kappa_2 v_x(t, s(t)) = s'(t)v(t, s(t)) \quad \text{for } 0 < t < T,$$

$$(1.7) \quad s(0) = s_0 \text{ and } u(0, x) = u_0, v(0, x) = v_0 \quad \text{for } 0 < x < s_0,$$

where κ_1 (resp. κ_2) is a diffusion constant of CO_2 in air (resp. water), $f(u, v) := \beta(\gamma v - u)$ is an effective Henry's law, where β and γ are positive constants, g and h are given functions corresponding to boundary conditions for u and v , respectively, $\psi(r) := \alpha[r]^+|^p$ for $r \in \mathbb{R}$ describes the rate of the carbonation reaction, where $p \geq 1$ and α is a positive constant². $s_0 \geq 0$ is the initial position of the free boundary, while u_0 and v_0 are the initial concentrations.

First mathematical models with free boundaries for describing the concrete carbonation process have been proposed by Muntean and Böhm in [14, 16], where the first mathematical results concerning the global existence and uniqueness of weak solutions as well as the stability of the solutions with respect to data and parameters

²The exponent p is sometimes called order of the chemical reaction, while the parameter α is just a proportionality constant. Its sensitivity with respect to the model output (s, u, v) has been studied numerically in [17].

have been investigated. Recently, we have improved their results by focussing a reduced free-boundary model still able to capturing the basic features of the carbonation process; see [2] for the reduced model and [1, 3] for the list of the new theorems on the existence and uniqueness of weak solutions to P. This model is in some sense minimal: It includes the transport of species (diffusion), their averaged transfer across air-water interfaces (the Henry law), as well as fast reaction (with an indefinitely large chemical compound - "the concrete"). We have used further the advantageous structure of the reduced model to study the large-time behavior of the penetration depths. Basically, we started to wonder whether the experimentally known \sqrt{t} -law

$$s(t) = \bar{C}\sqrt{t} \text{ for } t > 0,$$

where \bar{C} is a positive constant, is true or not [18]. Let us comment a bit on the context: It was shown in [22] (pp. 193-199) that the carbonation front behaves like a similarity solution to a one-phase Stefan-like problem [19]. Using matched-asymptotics techniques, the fast-reaction limit (for large Thiele moduli) done in [15] for a reaction-diffusion system also led to a \sqrt{t} -behavior of the carbonation front supporting experimental results from [12, 13], e.g. On the other hand, experimental

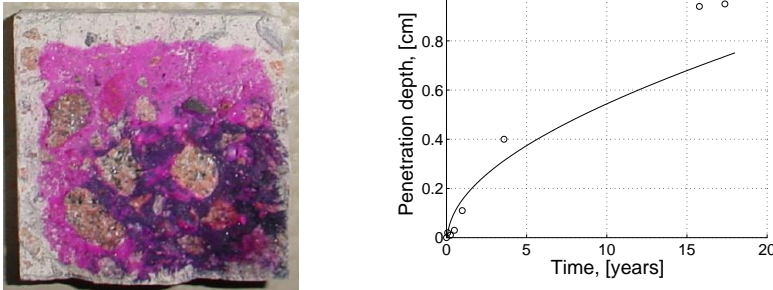


FIG. 1.1. (Left) Typical result of the phenolphthalein test on a partially carbonated sample (Courtesy of Prof. Dr. Max Setzer, University of Duisburg-Essen, Germany). The dark region indicates the uncarbonated part, while the brighter one points out the carbonated part. The two regions are separated by a sharp interface moving inwards the material. In this colorimetric test, this macroscopic interface corresponds to a drop in pH below 10. (Right) Computed interface positions vs. measured penetration depths [17].

results from [20] indicate that, depending on the type of the cement, a variety of t^β

front behaviors with $\beta \neq \frac{1}{2}$ are possible. Furthermore, Souplet, Fila and collaborators (compare [21, 7]) have shown that, under certain conditions, non-homogeneous Stefan-like problem can lead to asymptotics like $s(t) \sim t^{\frac{1}{3}}$. Somehow, the major question remains:

What is the correct asymptotics of the carbonation front propagation?

The main result of our preliminary investigations (based on the reduced FBP) is reported in [4] and supports the fact that

$$s(t) \rightarrow \infty \text{ as } t \rightarrow \infty \text{ and } s(t) \leq C'\sqrt{t} \text{ for } t \geq 0,$$

where C' is a positive constant. Moreover, in this paper we establish a result on the lower estimate for the free boundary s as follows: For some positive constant c

$$(1.8) \quad s(t) \geq c\sqrt{t} \text{ for } t \geq 0.$$

This estimate combined with the corresponding lower one would immediately guarantee the correctness of the \sqrt{t} -law from a mathematical modeling point of view. In section 2 we derive the missing lower bound.

Note that since, generally, $k_1 \gg k_2$ and $\gamma v \neq u$, the system (1.1)–(1.7) cannot be reduced to a scalar equation, where the use of Green functions representation [5, 19] would very much facilitate the obtaining of non-trivial lower bounds on concentrations, and hence, on the free boundary velocity. Furthermore, by using the similar method as the one used in the proof of (1.8), we can construct a weak solution to P satisfying $s_0 = 0$. It is worth mentioning that Fasano and Primicerio (cf. [8], e.g.) have investigated a one-phase Stefan problem when the measure of the initial domain vanishes. In their proof the comparison principle is used in an essential manner. However, for our problem P we do not have any comparison theorem for the free boundary. Our idea here is to develop a method to obtain improved uniform estimates for solutions and then use these estimates to prove the existence of weak solutions for the case $s_0 = 0$. This program is realized in section 3. There are neither physical nor mathematical reasons to believe that uniqueness of weak solutions for the case $s_0 = 0$ would not hold. However, since our fixing-domain technique is not applicable anymore, the uniqueness seems to be difficult to prove.

2. Large-time behavior of the free boundary. In order to give a statement of our result on the large-time behavior of (weak) solutions, we consider the problem P posed in the cylindrical domain $Q(T) := (0, T) \times (0, 1)$. To this end, we use the following change of variables:

Let

$$(2.1) \quad \bar{u}(t, y) = u(t, s(t)y) \text{ and } \bar{v}(t, y) = v(t, s(t)y) \text{ for } (t, y) \in Q(T).$$

Then, it holds that

$$\begin{aligned} \bar{u}_t - \frac{\kappa_1}{s^2} \bar{u}_{yy} - \frac{s'}{s} y \bar{u}_y &= f(\bar{u}, \bar{v}) \quad \text{in } Q(T), \\ \bar{v}_t - \frac{\kappa_2}{s^2} \bar{v}_{yy} - \frac{s'}{s} y \bar{v}_y &= -f(\bar{u}, \bar{v}) \quad \text{in } Q(T), \\ \bar{u}(0, t) &= g(t), \bar{v}(0, t) = h(t) \quad \text{for } 0 < t < T, \\ s'(t) &= \psi(\bar{u}(t, 1)) \quad \text{for } 0 < t < T, \\ -\frac{\kappa_1}{s(t)} \bar{u}_y(t, 1) &= s'(t) \bar{u}(t, 1) + s'(t) \quad \text{for } 0 < t < T, \end{aligned}$$

$$\begin{aligned}
-\frac{\kappa_2}{s(t)}\bar{v}_y(t, 1) &= s'(t)\bar{v}(t, 1) \quad \text{for } 0 < t < T, \\
s(0) &= s_0, \bar{u}(0, y) = \bar{u}_0(y), \bar{v}(0, y) = \bar{v}_0(y) \quad \text{for } 0 < y < 1,
\end{aligned}$$

where $\bar{u}_0(y) = u_0(s_0y)$ and $\bar{v}_0(y) = v_0(s_0y)$ for $y \in [0, 1]$.

For simplicity, we introduce some notations as follows: $H := L^2(0, 1)$, $X := \{z \in H^1(0, 1) : z(0) = 0\}$, X^* is the dual space of X ,

$$V(T) := L^\infty(0, T; H) \cap L^2(0, T; H^1(0, 1))$$

and

$$V_0(T) := V(T) \cap L^2(0, T; X),$$

and $(\cdot, \cdot)_H$ and $\langle \cdot, \cdot \rangle_X$ denote the usual inner product of H and the duality pairing between X and X^* , respectively.

First of all, we define a weak solution of $P(s_0, u_0, v_0, g, h)$. To do this, we use a similar concept of weak solution as the one introduced in [1].

DEFINITION 2.1. *Let s be a function on $[0, T]$ and u, v be functions on $Q_s(T)$ for $0 < T < \infty$, and \bar{u} and \bar{v} be functions defined by (2.1). We call that a triplet $\{s, u, v\}$ is a weak solution of P on $[0, T]$ if the conditions (S1) \sim (S5) hold:*

- (S1) $s \in W^{1,\infty}(0, T)$ with $s > 0$ on $[0, T]$, $(\bar{u}, \bar{v}) \in (W^{1,2}(0, T; X^*) \cap V(T) \cap L^\infty(Q(T)))^2$.
- (S2) $\bar{u} - g, \bar{v} - h \in L^2(0, T; X)$, $u(0) = u_0$ and $v(0) = v_0$.
- (S3) $s'(t) = \psi(u(t, s(t)))$ for a.e. $t \in [0, T]$ and $s(0) = s_0$.

$$(S4) \quad \int_0^T \langle \bar{u}_t, z \rangle_X dt + \int_{Q(T)} \frac{\kappa_1}{s^2} \bar{u}_y z_y dy dt + \int_0^T \frac{s'}{s} (\bar{u}(\cdot, 1) + 1) z(\cdot, 1) dt$$

$$= \int_{Q(T)} (f(\bar{u}, \bar{v}) + \frac{s'}{s} y \bar{u}_y) z dy dt \quad \text{for } z \in V_0(T).$$

$$(S5) \quad \int_0^T \langle \bar{v}_t, z \rangle_X dt + \int_{Q(T)} \frac{\kappa_2}{s^2} \bar{v}_y z_y dy dt + \int_0^T \frac{s'}{s} \bar{v}(\cdot, 1) z(\cdot, 1) dt$$

$$= \int_{Q(T)} (-f(\bar{u}, \bar{v}) + \frac{s'}{s} y \bar{v}_y) z dy dt \quad \text{for } z \in V_0(T).$$

Moreover, let s be a function on $[0, \infty)$, and u and v be functions on $Q_s := \{(t, x) | t > 0, 0 < x < s(t)\}$. We say that $\{s, u, v\}$ is a weak solution of P on $[0, \infty)$ if for any $T > 0$ the triplet $\{s, u, v\}$ is a weak solution of P on $[0, T]$.

Before recalling our results concerning the global existence and uniqueness of weak solutions to P on the time interval $[0, T]$, $T > 0$, we give the following assumptions for the involved data and model parameters:

- (A1) $f(u, v) = \beta(\gamma v - u)$ for any $(u, v) \in \mathbf{R}^2$ where β and γ are positive constants.
- (A2) $g, h \in W_{loc}^{1,2}([0, \infty)) \cap L^\infty(0, \infty)$, and $g \geq 0$ and $h \geq 0$ on $(0, \infty)$.
- (A3) $u_0 \in L^\infty(0, s_0)$ and $v_0 \in L^\infty(0, s_0)$ with $u_0 \geq 0$ and $v_0 \geq 0$ on $(0, s_0)$.

THEOREM 2.2. *(cf. [1, Theorems 1.1 and 1.2, Lemma 4.1]) If (A1) \sim (A3) hold, then P has one and only one weak nonnegative solution on $[0, \infty)$.*

The next theorem is the main result of this paper.

THEOREM 2.3. *If $g(t) = g_*$, $h(t) = h_*$ for $t \in [0, \infty)$, where g_* and h_* are positive constants with $\gamma h_* = g_*$, and (A1) and (A3) hold, then there exists a positive constant c such that*

$$s(t) \geq c\sqrt{t} \quad \text{for } t \geq 0.$$

The proof of Theorem 2.3 relies on three technical lemmas. We give these auxiliary results in the following.

LEMMA 2.4. *(cf. [4, Lemma 3.3]) If (A1) \sim (A3) hold, then a weak solution $\{s, u, v\}$ on $[0, \infty)$ satisfies*

$$\begin{aligned} & \int_0^{s(t)} xu(t)dx + \frac{1}{2}|s(t)|^2 + \kappa_1 \int_0^t u(\tau, s(\tau))d\tau \\ & + \int_0^{s(t)} xv(t)dx + \kappa_2 \int_0^t \int_0^{s(\tau)} v_x(\tau, x)dx d\tau \\ & = \int_0^{s_0} xu_0dx + \frac{1}{2}|s_0|^2 + \int_0^{s_0} xv_0dx + \kappa_1 \int_0^t g(\tau)d\tau \quad \text{for } t \geq 0. \end{aligned}$$

Proof. Let $T > 0$. In (S4) we can take $z(t) = s^2(t)y$ for $t \in [0, T]$ so that we have

$$\begin{aligned} & \int_0^T \langle \bar{u}_t(t), s^2(t)y \rangle_X dt + \int_{Q(T)} \kappa_1 \bar{u}_y(t) dy dt + \int_0^T s'(t)s(t)(\bar{u}(t, 1) + 1)dt \\ (2.2) \quad & = \int_{Q(T)} (yf(\bar{u}(t), \bar{v}(t)) + \frac{s'(t)}{s(t)}y^2 \bar{u}_y(t))s^2(t)dy dt. \end{aligned}$$

Here, we note that

$$\begin{aligned} & \int_0^T \langle \bar{u}_t(t), s^2(t)y \rangle_X dt \\ & = -2 \int_0^T \int_0^1 \bar{u}(t)s'(t)s(t)y dy dt + \int_0^1 \bar{u}(T)s^2(T)y dy - \int_0^1 \bar{u}(0)s^2(0)y dy \\ (2.3) \quad & = -2 \int_0^T \int_0^{s(t)} u(t) \frac{s'(t)}{s(t)} x dx dt + \int_0^{s(T)} u(T)x dx - \int_0^{s_0} u_0 x dx; \end{aligned}$$

$$(2.4) \quad \int_{Q(T)} \kappa_1 \bar{u}_y(t) dy dt = \kappa_1 \int_0^T (\bar{u}(t, 1) - g(t))dt;$$

$$(2.5) \quad \int_0^T \frac{s'(t)}{s(t)} (\bar{u}(t, 1) + 1) s^2(t) dt = \int_0^T s'(t)s(t)\bar{u}(t, 1)dt + \frac{1}{2}(s^2(T) - s_0^2);$$

and

$$\begin{aligned} & \int_{Q(T)} \frac{s'(t)}{s(t)} y^2 \bar{u}_y(t) s^2(t) dy dt \\ & = -2 \int_{Q(T)} s'(t)s(t)y \bar{u}(t) dy dt + \int_0^T s'(t)s(t)\bar{u}(t, 1)dt \\ (2.6) \quad & = -2 \int_{Q(T)} \frac{s'(t)}{s(t)} u(t) dx dt + \int_0^T s'(t)s(t)x \bar{u}(t, 1)dt. \end{aligned}$$

By substituting (2.3) \sim (2.6) into (2.2) we see that

$$\begin{aligned} & \int_0^{s(T)} xu(T)dx + \frac{1}{2}s^2(T) + \kappa_1 \int_0^T u(t, s(t))dt \\ &= \int_0^{s_0} xu_0dx + \frac{1}{2}s_0^2 + \kappa_1 \int_0^T g(t)dt + \int_{Q_s(T)} f(u, v)xdxdt. \end{aligned}$$

Similarly, it follows from (S5) with $z(t) = s^2(t)y$ that

$$\int_0^{s(T)} xv(T)dx + \kappa_2 \int_{Q_s(T)} v_x(\tau, x)dxdt = \int_0^{s_0} xv_0dx - \int_{Q_s(T)} f(u, v)xdxdt.$$

Adding these two equations leads to the end of the proof of this lemma. \square

Before starting off to providing a proof for the main result of the paper (Theorem 2.3), we wish to point out in Lemma 2.5 and in Lemma 2.6 below that our free-boundary problem allows for positive and uniformly bounded concentrations, and also, that an energy-like inequality holds.

LEMMA 2.5. (cf. [4, Lemma 3.2]) *Assume (A1) \sim (A3) hold, take positive numbers g^* and h^* satisfying $u_0 \leq g^*$, $v_0 \leq h^*$ on $[0, s_0]$, $g \leq g^*$, $h \leq h^*$ on $[0, \infty)$ and $g^* = \gamma h^*$, and let $\{s, u, v\}$ be a weak solution of P on $[0, \infty)$. Then it holds that*

$$0 \leq u \leq g^*, 0 \leq v \leq h^* \text{ on } Q_s.$$

LEMMA 2.6. (cf. [4, Lemma 3.4]) *Under the same assumptions as in Theorem 2.3 a weak solution $\{s, u, v\}$ of P on $[0, \infty)$ satisfies*

$$\begin{aligned} & \frac{1}{2} \int_0^{s(t)} |u(t) - g_*|^2 dx + \frac{\gamma}{2} \int_0^{s(t)} |v(t) - h_*|^2 dx + \frac{1}{2} \int_0^t |s'(\tau)|^{1+2/p} d\tau \\ & + \kappa_1 \int_0^t \int_0^{s(\tau)} |u_x(\tau)|^2 dx d\tau + \gamma \kappa_2 \int_0^t \int_0^{s(\tau)} |v_x(\tau)|^2 dx d\tau \\ & \leq \frac{1}{2} \int_0^{s_0} |u_0 - g_*|^2 dx + \frac{\gamma}{2} \int_0^{s_0} |v_0 - h_*|^2 dx \\ & + \int_0^t s'(\tau) \left(\frac{1}{2} |g_*|^2 + g_* + \frac{\gamma}{2} |h_*|^2 \right) d\tau \quad \text{for } t \geq 0. \end{aligned}$$

2.1. Proof of Theorem 2.3.. In this section, we give the proof of our main result.

Proof. Let $\{s, u, v\}$ be a weak solution of P on $[0, \infty)$, and g^* and h^* be positive constants defined in Lemma 2.5. First, Lemma 2.6 implies that

$$\begin{aligned} & \gamma \kappa_2 \int_0^t \int_0^{s(\tau)} |v_x(\tau)|^2 dx d\tau \\ & \leq \frac{1}{2} \int_0^{s_0} (|u_0 - g_*|^2 + \gamma |v_0 - h_*|^2) dx + \int_0^t s'(\tau) \left(\frac{1}{2} |g_*|^2 + g_* + \frac{\gamma}{2} |h_*|^2 \right) d\tau \\ & \leq \frac{1}{2} \int_0^{s_0} (|u_0 - g_*|^2 + \gamma |v_0 - h_*|^2) dx \\ & + \left(\frac{1}{2} |g_*|^2 + g_* + \frac{\gamma}{2} |h_*|^2 \right) (s(t) - s_0) \quad \text{for } t \geq 0. \end{aligned}$$

Hence, there is a positive constant depending on u_0, v_0, g_*, h_* and s_0 such that

$$\int_0^t \int_0^{s(\tau)} |v_x(\tau)|^2 dx d\tau \leq C_1 + C_1 s(t) \quad \text{for } t \geq 0.$$

Next, on account of Lemma 2.4 we see that

$$\begin{aligned} & \int_0^{s(t)} xu(t) dx + \frac{1}{2}|s(t)|^2 + \kappa_1 \int_0^t u(\tau, s(\tau)) d\tau \\ & + \int_0^{s(t)} xv(t) dx + \kappa_2 \int_0^t \int_0^{s(\tau)} v_x(\tau, x) dx d\tau \\ & = \int_0^{s_0} xu_0 dx + \frac{1}{2}|s_0|^2 + \int_0^{s_0} xv_0 dx + \kappa_1 \int_0^t g(\tau) d\tau \\ & \geq \kappa_1 g_* t \quad \text{for } t \geq 0. \end{aligned}$$

Here, we note that

$$u(t, s(t)) = \left(\frac{s'(t)}{\alpha}\right)^{1/p} \quad \text{for } t \geq 0.$$

Then, by putting $M = \max\{g^*, h^*\}$ we obtain

$$\begin{aligned} \kappa_1 g_* t & \leq 2M \int_0^{s(t)} x dx + \frac{1}{2}|s(t)|^2 + \frac{\kappa_1}{\alpha^{1/p}} \int_0^t (s'(\tau))^{1/p} d\tau \\ & + \kappa_2 \left(\int_{Q_s(t)} |v_x|^2 dx d\tau \right)^{1/2} \left(\int_{Q_s(t)} dx d\tau \right)^{1/2} \quad \text{for } t \geq 0. \end{aligned}$$

It is clear that

$$\begin{aligned} \frac{\kappa_1}{\alpha^{1/p}} \int_0^t (s'(\tau))^{1/p} d\tau & \leq \frac{\kappa_1}{\alpha^{1/p}} \left(\int_0^t s'(\tau) d\tau \right)^{1/p} t^{1-1/p} \\ & \leq \frac{\kappa_1}{\alpha^{1/p}} s(t)^{1/p} t^{1-1/p} \\ (2.7) \quad & \leq \frac{1}{4} \kappa_1 g_* t + C_2 s(t) \quad \text{for } t \geq 0, \end{aligned}$$

where C_2 is some positive constant, and

$$\begin{aligned} & \kappa_2 \left(\int_{Q_s(t)} |v_x|^2 dx d\tau \right)^{1/2} \left(\int_{Q_s(t)} dx d\tau \right)^{1/2} \\ & \leq \kappa_2 C_1^{1/2} (1 + s(t))^{1/2} t^{1/2} s(t)^{1/2} \\ & \leq \frac{1}{4} \kappa_1 g_* t + C_3 (s(t) + s(t)^2) \quad \text{for } t \geq 0, \end{aligned}$$

where C_3 is some positive constant.

From the above inequalities we can get

$$\frac{1}{2} \kappa_1 g_* t \leq (M + \frac{1}{2} + C_3) |s(t)|^2 + (C_2 + C_3) s(t) \quad \text{for } t \geq 0.$$

Now, let $t \geq 1$. In this case we see that

$$\frac{1}{2} \kappa_1 g_* t \leq (M + \frac{1}{2} + C_3) |s(t)|^2 + C_4 |s(t)|^2 + \frac{1}{4} \kappa_1 g_* t \quad \text{for } t \geq 0,$$

where C_4 is some positive constant. Thus it holds that

$$\left(\frac{\kappa_1 g_*}{4(M+1+C_3+C_4)} t \right)^{1/2} \leq s(t) \quad \text{for } t \geq 1.$$

In case $0 \leq t \leq 1$, we have $s_0 \sqrt{t} \leq s(t)$.

Therefore, by putting $\nu_0 = \min\{s_0, \left(\frac{\kappa_1 g_*}{4(M+1+C_3+C_4)} \right)^{1/2}\}$ we conclude that

$$\nu_0 \sqrt{t} \leq s(t) \quad \text{for } t \geq 0.$$

□

3. Appearance of a moving carbonation front – The case $s_0 = 0$. The aim of this section is to prove a result concerning the existence of weak solutions to P for the case $s_0 = 0$. This is the case when the free boundary starts off moving precisely from the outer boundary [exposed to CO_2]. Before giving the statement of the theorem, we denote for simplicity

$$C_0((0, T]; X) = \{z \in C([0, T] : X) : z = 0 \text{ on } [0, \delta_z) \text{ for some } \delta_z > 0\}.$$

THEOREM 3.1. *Let $T > 0$, and g and h be functions on $[0, T]$ satisfying $g, h \in W^{1,2}(0, T)$ and $g(t) \geq g_0 > 0$ and $h \geq 0$ for $t \in [0, T]$, where g_0 is a given positive constant. Then under (A1) there exists a triplet $\{s, u, v\}$ of functions such that $s \in W^{1,\infty}(0, T)$, $s(0) = 0$, $s(t) > 0$ for $t \in (0, T]$, $\bar{u}, \bar{v} \in L^\infty(Q(T))$, $\bar{u} - g, \bar{v} - h \in L^2(0, T; X)$, $\bar{u}, \bar{v} \in C((0, T]; H)$, $\bar{u}, \bar{v} \in W_{loc}^{1,2}((0, T]; X^*)$,*

$$(3.1) \quad s'(t) = \psi(\bar{u}(t, 1)) \quad \text{for a.e. } t \in [0, T],$$

$$(3.2) \quad \begin{aligned} & \int_0^T \langle \bar{u}_t, z \rangle_X dt + \int_{Q(T)} \frac{\kappa_1}{s^2} \bar{u}_y z_y dy dt + \int_0^T \frac{s'}{s} z(\cdot, 1) dt \\ &= \int_{Q(T)} \left(f(\bar{u}, \bar{v}) - \frac{s'}{s} y \bar{u}_y \right) z dy dt \quad \text{for } z \in C_0((0, T]; X), \end{aligned}$$

$$(3.3) \quad \begin{aligned} & \int_0^T \langle \bar{v}_t, z \rangle_X dt + \int_{Q(T)} \frac{\kappa_2}{s^2} \bar{v}_y z_y dy dt \\ &= - \int_{Q(T)} \left(f(\bar{u}, \bar{v}) + \frac{s'}{s} y \bar{v}_y \right) z dy dt \quad \text{for } z \in C_0((0, T]; X), \end{aligned}$$

where \bar{u} and \bar{v} are functions defined by (2.1).

Proof. First, let $\{s_{0n}\}$ be a sequence satisfying $s_{0n} > 0$ for each n and $s_{0n} \rightarrow 0$ as $n \rightarrow \infty$ and put $u_{0n} = g(0)$ and $v_{0n} = h(0)$ on $[0, s_{0n}]$. Then, Theorem 2.2 guarantees that $P(s_{0n}, u_{0n}, v_{0n}, g, h)$ has a unique weak solution $\{s_n, u_n, v_n\}$ on $[0, T]$. Here, we denote by \bar{u}_n and \bar{v}_n the functions defined by (2.1) with $s = s_n$, $u = u_n$ and $v = v_n$ for each n . Since we can take positive constants g^* and h^* such that $g \leq g^*$ and $h \leq h^*$ on $[0, T]$, $u_{0n} \leq g^*$ and $v_{0n} \leq h^*$ on $[0, s_{0n}]$ for n and $g^* = \gamma h^*$, Lemma 2.5 implies that

$$(3.4) \quad 0 \leq u_n \leq g^*, 0 \leq v_n \leq h^* \quad \text{on } Q_{s_n}(T) \text{ for any } n.$$

By (S3) and this shows that $|s'_n(t)| \leq \psi(g^*)$ for $t \in [0, T]$ and n so that the set $\{s_n\}$ is bounded in $W^{1,\infty}(0, T)$. Clearly, there exists a positive constant L_1 such that $0 \leq s_n(t) \leq L_1$ for $t \in [0, T]$ and n .

Next, the following estimate is a direct consequence of [1, Lemma 4.2]: For each n

$$\begin{aligned} & \kappa_1 \int_0^t \int_0^{s_n(\tau)} |u_{nx}|^2 dx d\tau + \kappa_2 \int_0^t \int_0^{s_n(\tau)} |v_{nx}|^2 dx d\tau \\ & \leq 2(C_f^2 + 1) \int_0^t \int_0^{s_n(\tau)} (|u_n(\tau) - g(\tau)|^2 + |v_n(\tau) - h(\tau)|^2) dx d\tau \\ & \quad + 2 \int_0^t s_n(\tau) (|f(g(\tau), h(\tau))|^2 + |g_\tau(\tau)|^2 + |h_\tau(\tau)|^2) d\tau \\ & \quad + \int_0^t s'_n(\tau) (3|g(\tau)|^2 + |g(\tau)| + |h(\tau)|^2) d\tau \quad \text{for } t \in [0, T], \end{aligned}$$

where $C_f := \beta\gamma$. Because of the boundedness of $\{s_n\}$ and (3.4) there exists a positive constant M_2 such that

$$\int_0^T \int_0^{s_n(\tau)} |u_{nx}|^2 dx d\tau + \int_0^T \int_0^{s_n(\tau)} |v_{nx}|^2 dx d\tau \leq M_2 \text{ for } n.$$

Then, easily, we can obtain that $\{\bar{u}_{ny}\}$ and $\{\bar{v}_{ny}\}$ are bounded in $L^2(Q(T))$.

From now on we provide the estimate from below for the free boundary as follows.

To do so from Lemma 2.4 it follows that

$$\begin{aligned} \kappa_1 g_0 t & \leq \int_0^{s_n(t)} x u_n(t) dx + \frac{1}{2} |s_n(t)|^2 + \kappa_1 \int_0^t u_n(\tau, s_n(\tau)) d\tau \\ & \quad + \int_0^{s_n(t)} x v_n(t) dx + \kappa_2 \int_0^t \int_0^{s_n(\tau)} v_{nx}(\tau, x) dx d\tau \\ & =: J_{1n}(t) + J_{2n}(t) + J_{3n}(t) + J_{4n}(t) + J_{5n}(t) \quad \text{for } t \geq 0 \text{ and } n. \end{aligned}$$

Here, it is obvious that

$$\left. \begin{aligned} J_{1n}(t) + J_{4n}(t) & \leq \frac{1}{2} (g^* + h^*) |s_n(t)|^2 \\ J_{5n}(t) & \leq \kappa_2 M_2^{1/2} (t s_n(t))^{1/2} \end{aligned} \right\} \text{ for } t \in [0, T] \text{ and } n.$$

Similarly to (2.7), by using (1.4) we observe that

$$J_{3n}(t) \leq \frac{\kappa_1}{\alpha^{1/p}} \int_0^t |s'_n(\tau)|^{1/p} d\tau \leq \frac{\kappa_1 T^{1-1/p}}{\alpha^{1/p}} s_n(t)^{1/p} \text{ for } t \in [0, T] \text{ and } n.$$

From the above inequalities we have

$$\begin{aligned} & \kappa_1 g_0 t \\ & \leq \frac{g^* + h^* + 1}{2} s_n(t)^2 + \frac{\kappa_1 T^{1-1/p}}{\alpha^{1/p}} s_n(t)^{1/p} + \kappa_2 (M_2 T)^{1/2} s_n(t)^{1/2} \\ & \leq \left(\frac{g^* + h^* + 1}{2} L_1^{2-\mu} + \frac{\kappa_1 T^{1-1/p}}{\alpha^{1/p}} L_1^{1/p-\mu} + \kappa_2 (M_2 T)^{1/2} L_1^{1/2-\mu} \right) s_n(t)^\mu \\ & =: M_3 s_n(t)^\mu \text{ for } t \in [0, T] \text{ and } n, \end{aligned}$$

where

$$\mu := \min\{1/p, 1/2\}$$

so that

$$(3.5) \quad s_n(t) \geq \nu_1 t^{1/\mu} \text{ for } t \in [0, T] \text{ and } n,$$

where ν_1 is a positive constant independent of n .

As next step, we wish to estimate the time derivative of \bar{u}_n . Let $\delta > 0$ and $\eta \in L^2(\delta, T; X)$. Then (S4) implies that

$$\begin{aligned} & \left| \int_{\delta}^T \langle \bar{u}_{nt}(t), \eta(t) \rangle_X dt \right| \\ & \leq \left| \int_{\delta}^T \frac{\kappa_1}{s_n^2(t)} (\bar{u}_y(t), \eta_y(t))_H dt \right| + \left| \int_{\delta}^T \left(\frac{s'_n(t)}{s_n(t)} \bar{u}_n(t, 1) + \frac{s'_n(t)}{s_n(t)} \right) \eta(t, 1) dt \right| \\ & \quad + \left| \int_{\delta}^T (f(\bar{u}_n(t), \bar{v}_n(t)), \eta(t))_H dt \right| + \left| \int_{\delta}^T \frac{s'_n(t)}{s_n(t)} (y \bar{u}_{ny}(t), \eta(t))_H dt \right| \\ & =: I_{1n} + I_{2n} + I_{3n} + I_{4n}. \end{aligned}$$

Obviously, on account of (3.5) it holds that

$$\begin{aligned} I_{1n} & \leq \kappa_1 \int_{\delta}^T \frac{1}{\nu_1^2 t^{2/\mu}} |\bar{u}_{ny}(t)|_H |\eta_y(t)|_H dt \\ & \leq \frac{\kappa_1}{\nu_1^2 \delta^{2/\mu}} |\bar{u}_{ny}|_{L^2(\delta, T; H)} |\eta_y(t)|_{L^2(\delta, T; H)}; \end{aligned}$$

$$I_{2n} \leq \frac{\psi(g^*)}{\mu_1 \delta^{1/\mu}} (|\bar{u}_n|_{L^2(0, T; H^1(0, 1))} + T^{1/2}) |\eta|_{L^2(\delta, T; X)};$$

$$I_{3n} \leq \beta(\gamma h^* + g^*) T^{1/2} |\eta|_{L^2(\delta, T; X)};$$

$$I_{4n} \leq \frac{\psi(g^*)}{\nu_1 \delta^{1/\mu}} |\bar{u}_{ny}|_{L^2(0, T; H)} |\eta|_{L^2(\delta, T; X)} \quad \text{for } n.$$

Hence, the set $\{\bar{u}_{nt}\}$ and $\{\bar{v}_{nt}\}$ are bounded in $L^2(\delta, T; X^*)$ for each $\delta > 0$.

From these estimates we can take a subsequence $\{n_j\} \subset \{n\}$ satisfying $s_{n_j} \rightarrow s$ weakly* in $W^{1, \infty}(0, T)$ and $C([0, T])$, and $\bar{u}_{n_j} \rightarrow \bar{u}$ and $\bar{v}_{n_j} \rightarrow \bar{v}$ weakly* in $L^\infty(Q(T))$ and weakly in $L^2(0, T; H^1(0, 1))$, in $C([\delta, T]; H)$ and weakly in $W^{1, 2}(\delta, T; X^*)$ for each $\delta > 0$ as $j \rightarrow \infty$, where $s \in W^{1, \infty}(0, T)$, $\bar{u}, \bar{v} \in L^\infty(Q(T))$, $\bar{u} - g, \bar{v} - h \in L^2(0, T; X)$ and

$$\bar{u}, \bar{v} \in C((0, T]; H) \cap W_{loc}^{1, 2}((0, T]; X^*).$$

By (3.5) we have $s(t) > 0$ for $t > 0$. Also, $s(0) = 0$.

In order to complete the proof of the Theorem, it is necessary to show that (3.2), (3.3) and (3.1) hold. Let $\eta \in C_0((0, T]; X)$. Then $\eta = 0$ on $[0, \delta]$ for some $\delta > 0$. By taking $z = \eta$ in (S4) we infer that

$$\begin{aligned}
& \int_{\delta}^T \langle \bar{u}_{n_j t}(t), \eta(t) \rangle_X dt + \int_{\delta}^T \frac{\kappa_1}{s_{n_j}^2(t)} (\bar{u}_{n_j y}(t), \eta_y(t))_H dt \\
& + \int_{\delta}^T \left(\frac{s'_{n_j}(t)}{s_{n_j}(t)} \bar{u}_{n_j}(t, 1) + \frac{s'_{n_j}(t)}{s_{n_j}(t)} \right) \eta(t, 1) dt \\
& = \int_{\delta}^T (f(\bar{u}_{n_j}(t), \bar{v}_{n_j}(t)) + \frac{s'_{n_j}(t)}{s_{n_j}(t)} y \bar{u}_{n_j y}(t), \eta(t))_H dt \quad \text{for } j.
\end{aligned}$$

Elementary calculations yield:

$$(3.6) \quad \bar{u}_{n_j}(\cdot, 1) \rightarrow \bar{u}(\cdot, 1) \text{ in } L^4(\delta, T) \text{ as } j \rightarrow \infty$$

so that

$$\int_{\delta}^T \frac{s'_{n_j}(t)}{s_{n_j}(t)} \bar{u}_{n_j}(t, 1) \eta(t, 1) dt \rightarrow \int_{\delta}^T \frac{s'(t)}{s(t)} \bar{u}(t, 1) \eta(t, 1) dt \quad \text{as } j \rightarrow \infty.$$

Moreover, we can obtain $s'_{n_j} \rightarrow s'$ in $L^4(\delta, T)$ as $j \rightarrow \infty$ and

$$\int_{\delta}^T \left(\frac{s'_{n_j}(t)}{s_{n_j}(t)} y \bar{u}_{n_j y}(t), \eta(t) \right)_H dt \rightarrow \int_{\delta}^T \left(\frac{s'(t)}{s(t)} y \bar{u}_y(t), \eta(t) \right)_H dt \text{ as } j \rightarrow \infty.$$

Therefore, we can prove that (3.2) holds. Similarly, (3.3) is valid. Finally, by (3.6) we get (3.1). Thus the proof of this theorem has been finished. \square

A practical comment. Before using in the engineering practice the \sqrt{t} information for forecasting purposes, the practitioner should be aware of the fact that its validity is closely related to the validity of the underlying free-boundary model P. Relying on our working experience with such FBPs for carbonation (based on [17], e.g.), we can say that P captures well accelerated carbonation tests, but it may not be suitable for predicting the evolution of carbonation scenarios under natural exposure conditions.

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